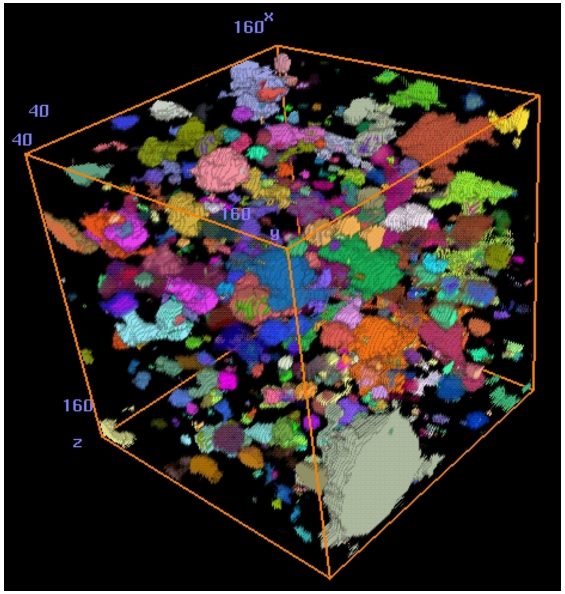
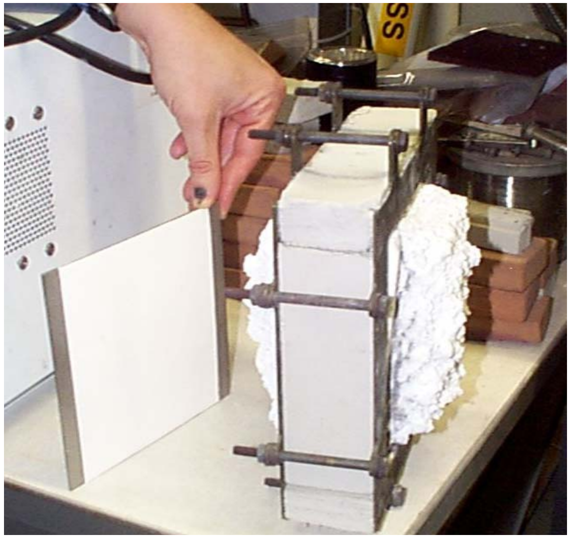
Fire Resistive Materials for Structural Steel





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NIST/BFRL Annual Fire Conference

April 3, 2006

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

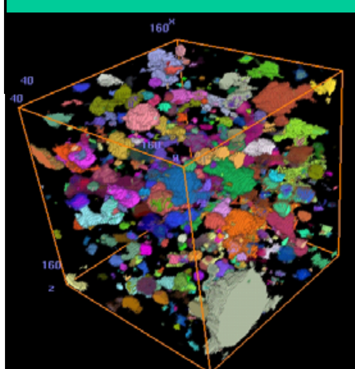
Background

- Events of 9/11 and subsequent WTC investigation have highlighted the importance of fire resistive materials (FRMs) in their role of limiting the temperature rise of structural steel
- R&D project on FRMs included in the Safety of Threatened Buildings program
  - Joint between 861.05 and 861.06 (Inorganic and Polymeric Materials)
  - Objective is to apply materials science to understanding and **improving** FRM performance
    - Develop linkages between microstructure and performance properties
  - The two most critical performance properties are adhesion/cohesion (does it stay on/up?) and thermal conductivity (does it keep the steel cool?)

Microstructure
Experimental
3-D Tomography
2-D optical, SEM
Confocal microscopy

Modeling
3-D Reconstruction

Parameters
Porosity
Pore Sizes
Contact Areas



Properties
(all as a function of T)
Thermal
Heat Capacity
Conductivity
Density
Heats of Reaction

Adhesion
Pull-off strength
Peel strength
Adhesion energy
Fracture toughness

Equipment
TGA/DSC/STA
Hot Disk®
Slug calorimeter

Environmental
Interior
Temperature, RH, load

Exterior
Temperature, RH, UV, load

Performance Prediction
Lab scale testing
ASTM E119 Test
Real structures (WTC)

Materials Science-Based Studies of Fire Resistive Materials

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Types of Materials

- Spray-applied FRMs (thick --- 25 mm to 50 mm)
  - Low density products (200 to 350 kg/m^3)
    - Mineral fibers with portland cement binder
      - Mixed dry with water applied at the spray nozzle
    - Gypsum-based with lightweight fillers
      - Vermiculite or expanded polystyrene beads as fillers
      - Mixed with water and then sprayed
  - Medium and high density products (400 to 700 kg/m^3)
    - Generally portland cement-based
- Thin film intumescents
  - Organics that expand up to 40 X at around 200 ^oC
  - Inorganics, typically with less expansion
- Rigid board products, wraps, etc.
  - Calcium silicate-based binder
  - Blended gypsum/portland cement binders

Focus: Test Method Development

- FRMs are currently characterized by **room temperature** properties such as pull-off adhesion/cohesion strength, density, and thermal conductivity
- However, it is really the values of these properties at **high temperatures** which will determine the performance of FRMs during a fire exposure
- Adequate test methods for property quantification at high temperatures do not exist or are inadequate for FRMs so our starting point and current focus has been development of high temperature test methods

Marshmallows are sticky and expand at high temperatures; Potential FRM???

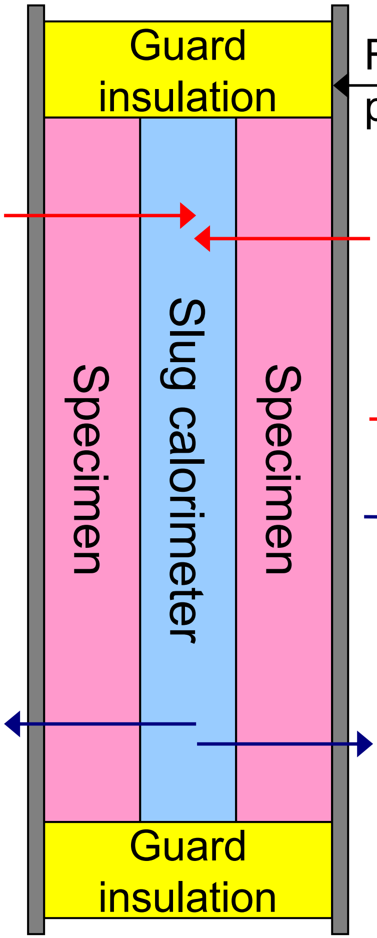
Thermal Conductivity at High Temperatures

- How to measure it?
  - ASTM C1113: Hot wire method
    - Difficult to maintain contact with porous FRM specimens
    - No information on influences of reactions, phase changes, etc.
  - High-temperature guarded hot plate
    - Steady-state method (no info on reactions, etc.)
    - State-of-the art facility under construction in BFRL at NIST
  - Transient plane source method (Hot Disk®)
    - Unit with furnace (test up to 700 ^{o}C) at BFRL
  - Slug calorimeter (designed and built at BFRL in 2004 and used extensively since then)
    - Similar in principle to the Cenco-Fitch Apparatus used in ASTM D2214 for estimating the thermal conductivity of leather (first published by Fitch in 1935)
    - Using multiple heating/cooling scans provides valuable information on the influences of reactions, etc.

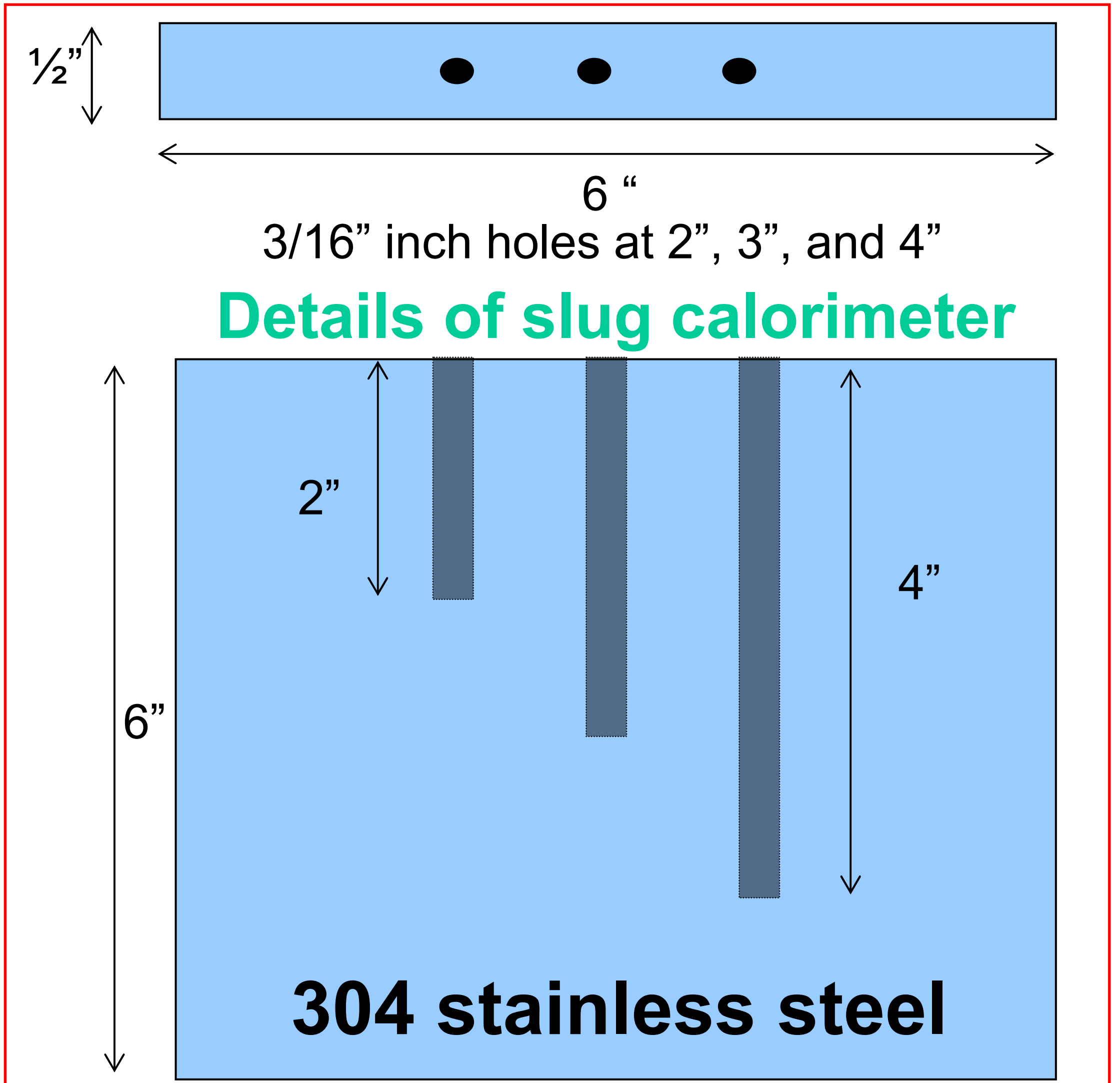
Slug Calorimeter Technique

- Sandwich specimen consisting of two “slabs” of FRM covering two sides of a steel slug of known mass and heat capacity
- Monitor slug temperature change as entire sandwich is exposed to a heating/cooling cycle
- Calculate effective thermal conductivity during **multiple** heating/cooling cycles
- For detailed information see: Bentz, D.P., Flynn, D.R., Kim, J.H., and Zarr, R.R., “A Slug Calorimeter for Evaluating the Thermal Performance of Fire Resistive Materials,” accepted by *Fire and Materials*, 2005, available in electronic monograph at http://ciks.cbt.nist.gov/garbocz/slugpaper1.

Slug Calorimeter

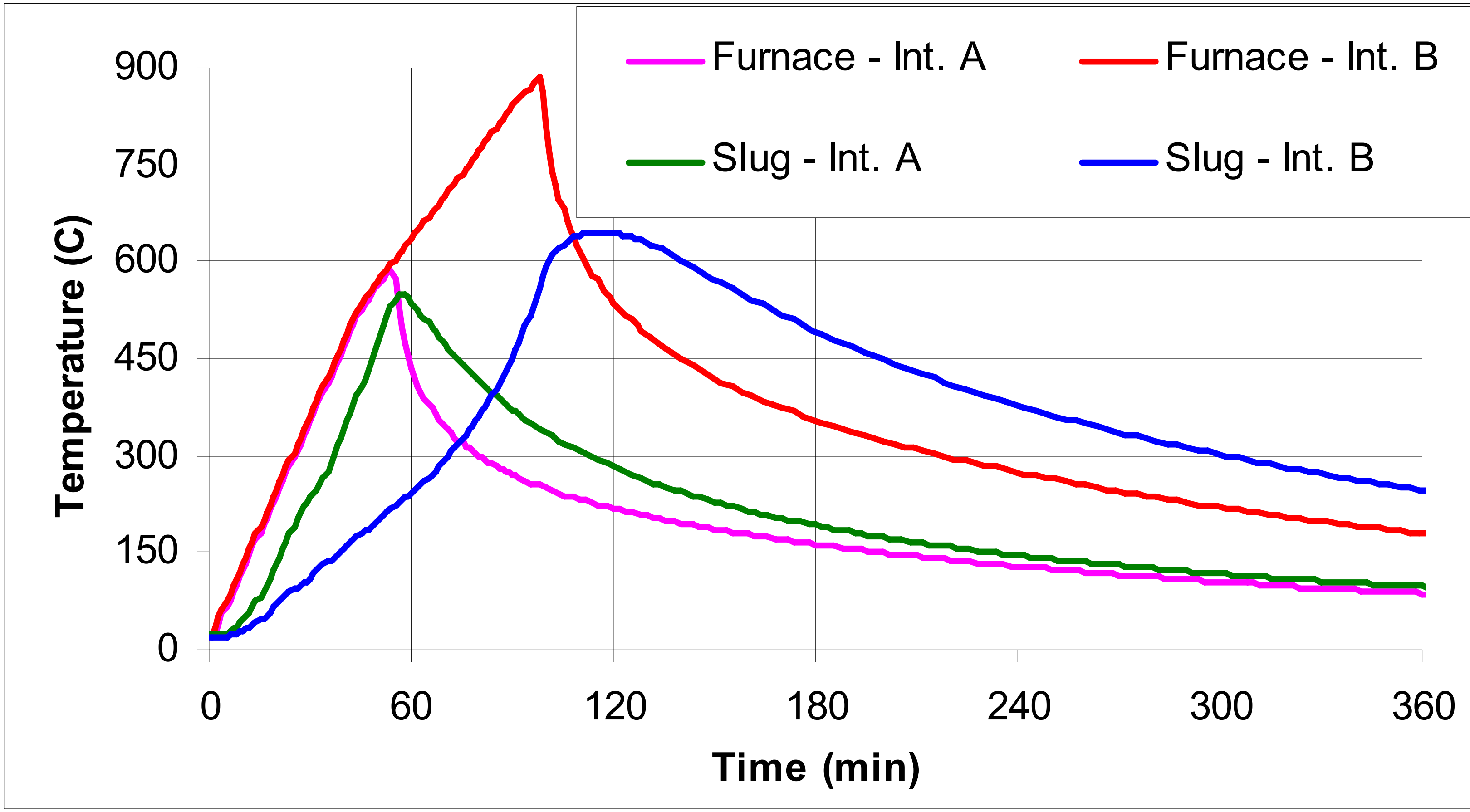


Experimental setup



Details of slug calorimeter

Raw Data for Exposure of Intumescents



Time for central slug to reach 538 °C varied from 52 minutes to 96 minutes for the two different materials

Determination of Effective k

(courtesy of Dan Flynn, BFRL guest researcher)

$$\partial^2 T / \partial z^2 = (1/\alpha)(\partial T/\partial t)$$

With B.C.: $T(0,t)=Ft$, $k(\partial T/\partial z) + H(\partial T/\partial t)=0$

α is the thermal diffusivity

H is the thermal capacity of one half of the slug plate

F is the rate of temperature increase/decrease of the slug

$$\text{Solution: } T(z,t)=F[t-(H+lC)z/k+Cz^2/(2k)]$$

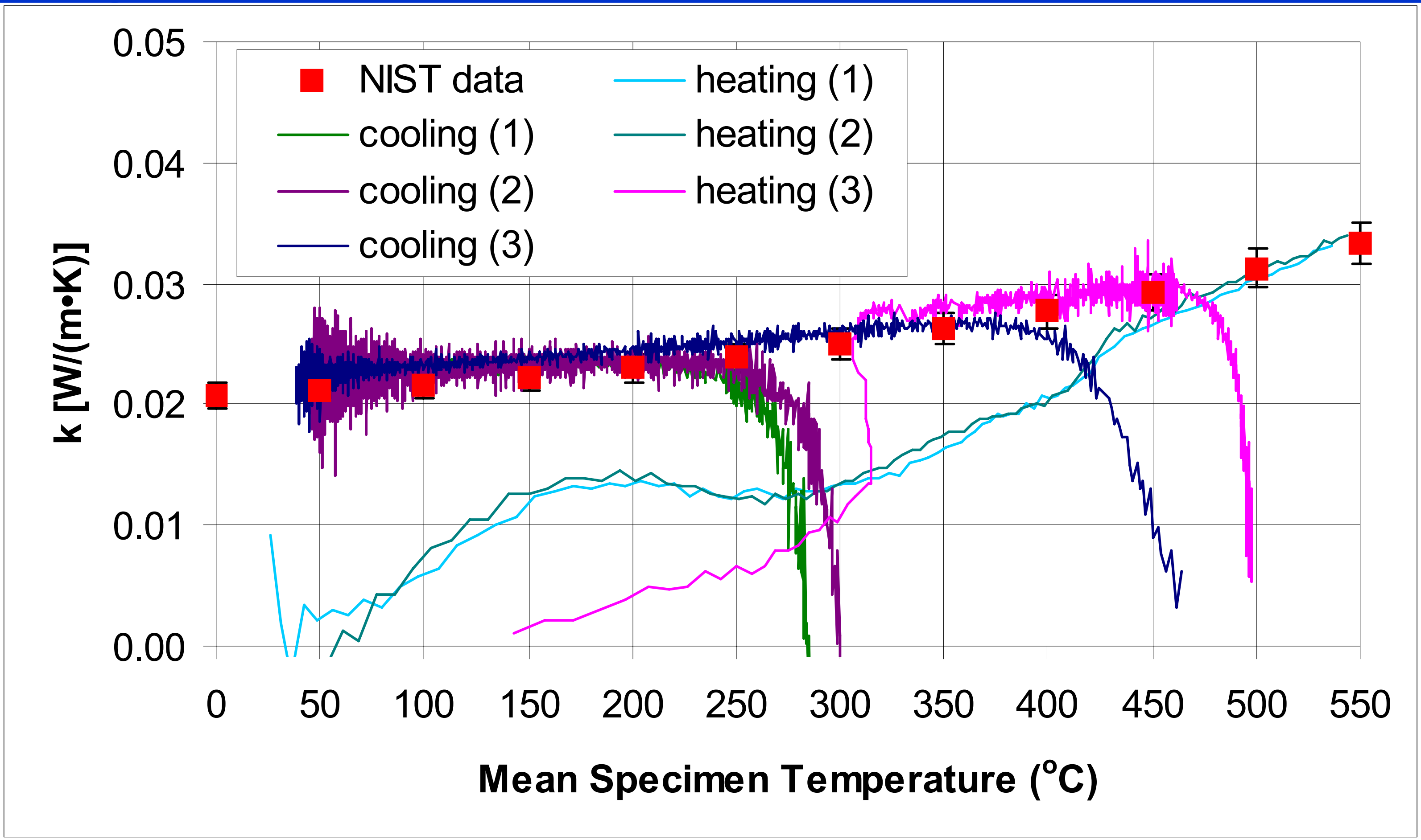
l is the specimen thickness, C its volumetric heat capacity

$$\Delta T = (Fl/k)*[H+lC/2]$$

ΔT is the temperature difference across the specimen

$$k=Fl(H+lC/2)/\Delta T=Fl(M_S c_p^{S}+M_{FRM} c_p^{FRM})/2A\Delta T$$

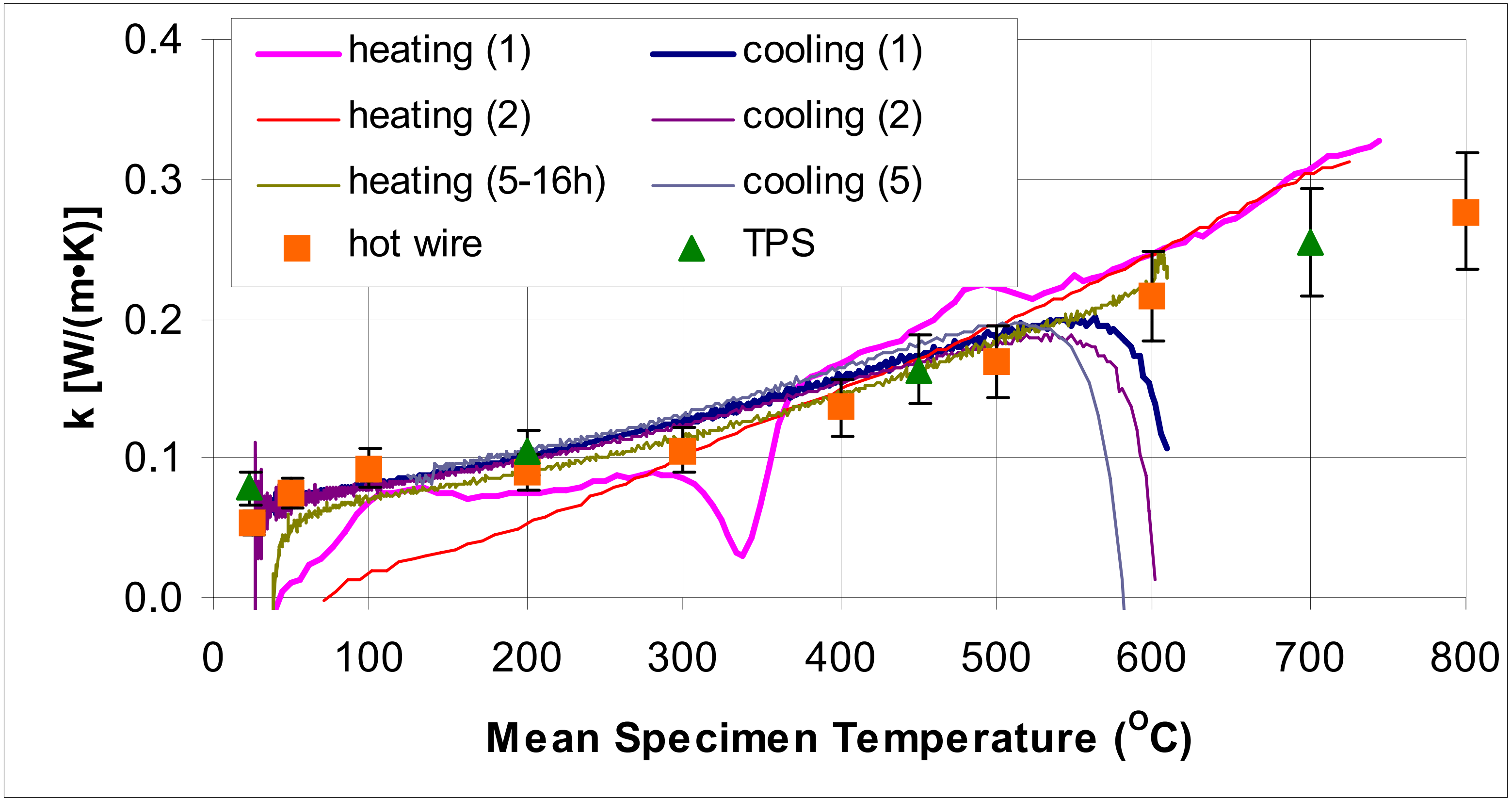
Slug Calorimeter Results: Fumed Silica Board



-Results for (non-reactive) fumed silica board in good agreement with previous NIST guarded hot plate (1988) measurements

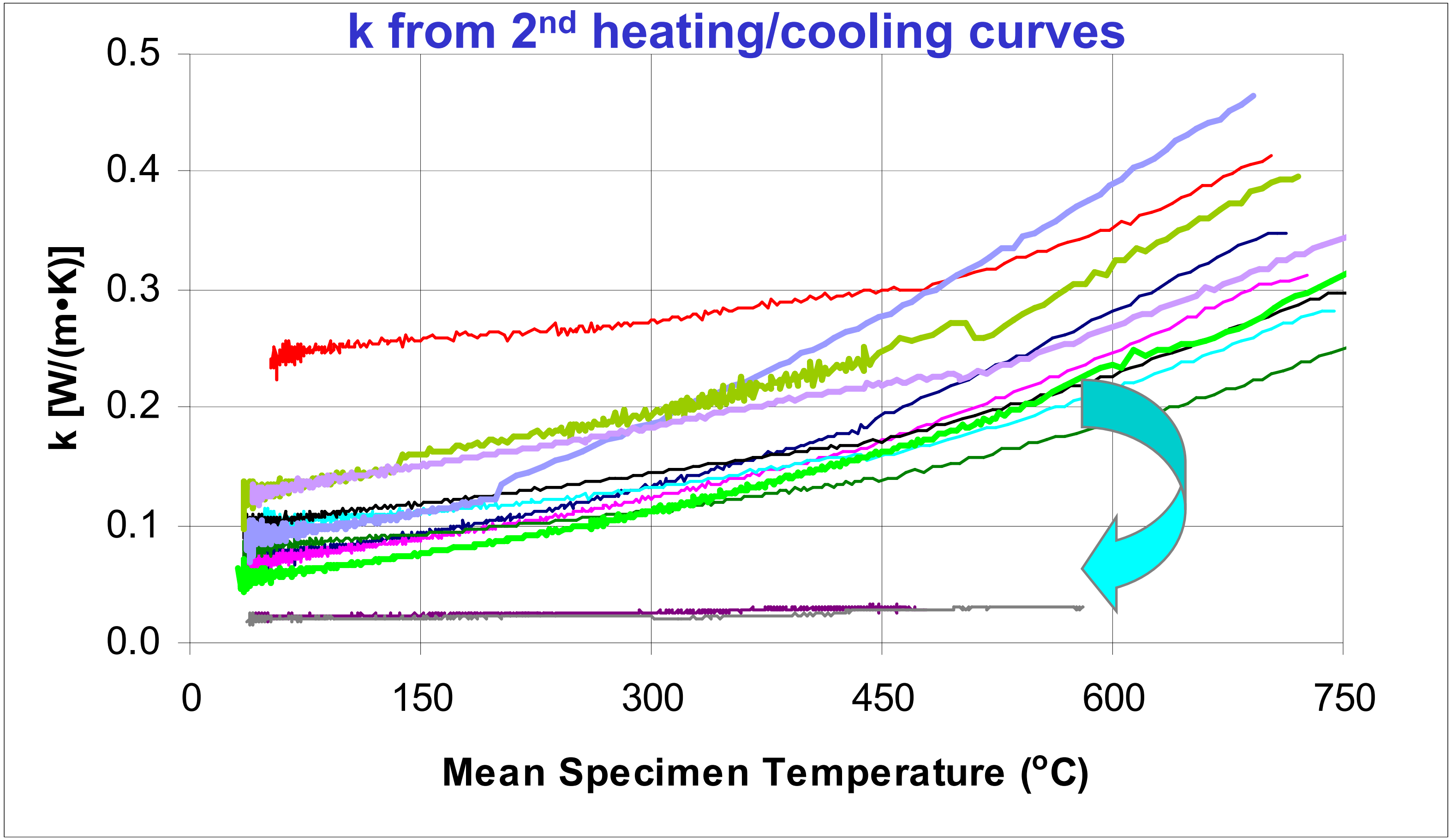
-Extremely low k at all temperatures [contains an opacifier and nanometer-sized particles (about 10 nm)]

Slug Calorimeter Results: FRM A



- Good agreement with previously measured values
- Good repeatability in cooling curves for different runs
- Differences between 1st and 2nd heating cycle provide valuable information on influences of endothermic and exothermic events, including reactions, phase changes, and mass transfer

Slug Calorimeter Results: Comparison



- High variability between different FRMs especially at higher T
- High T insulation boards (two lower curves) have effective k values significantly lower than current FRMs and exhibit minimal increases at higher temperatures

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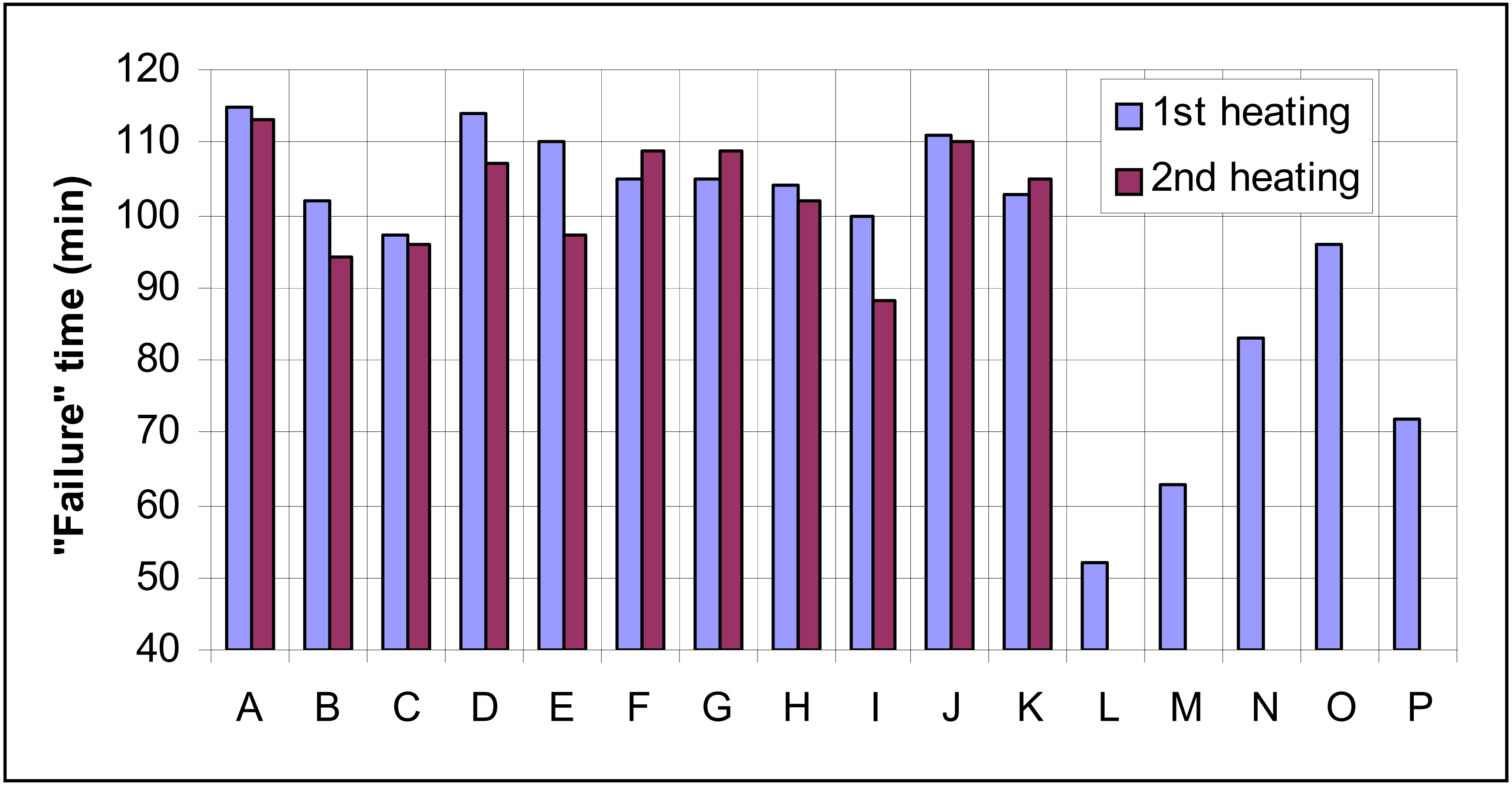
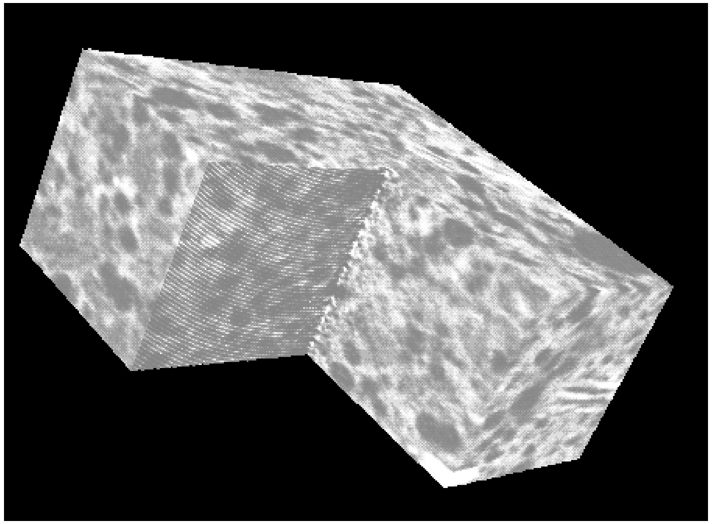
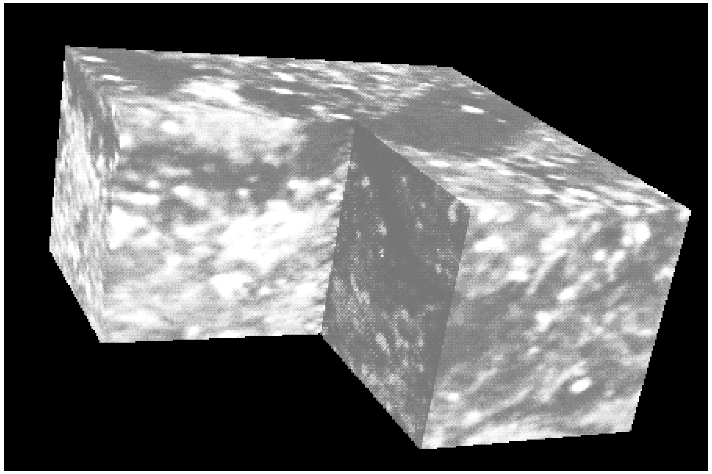
Comparison of Time for Steel Slug to Reach 538 °C



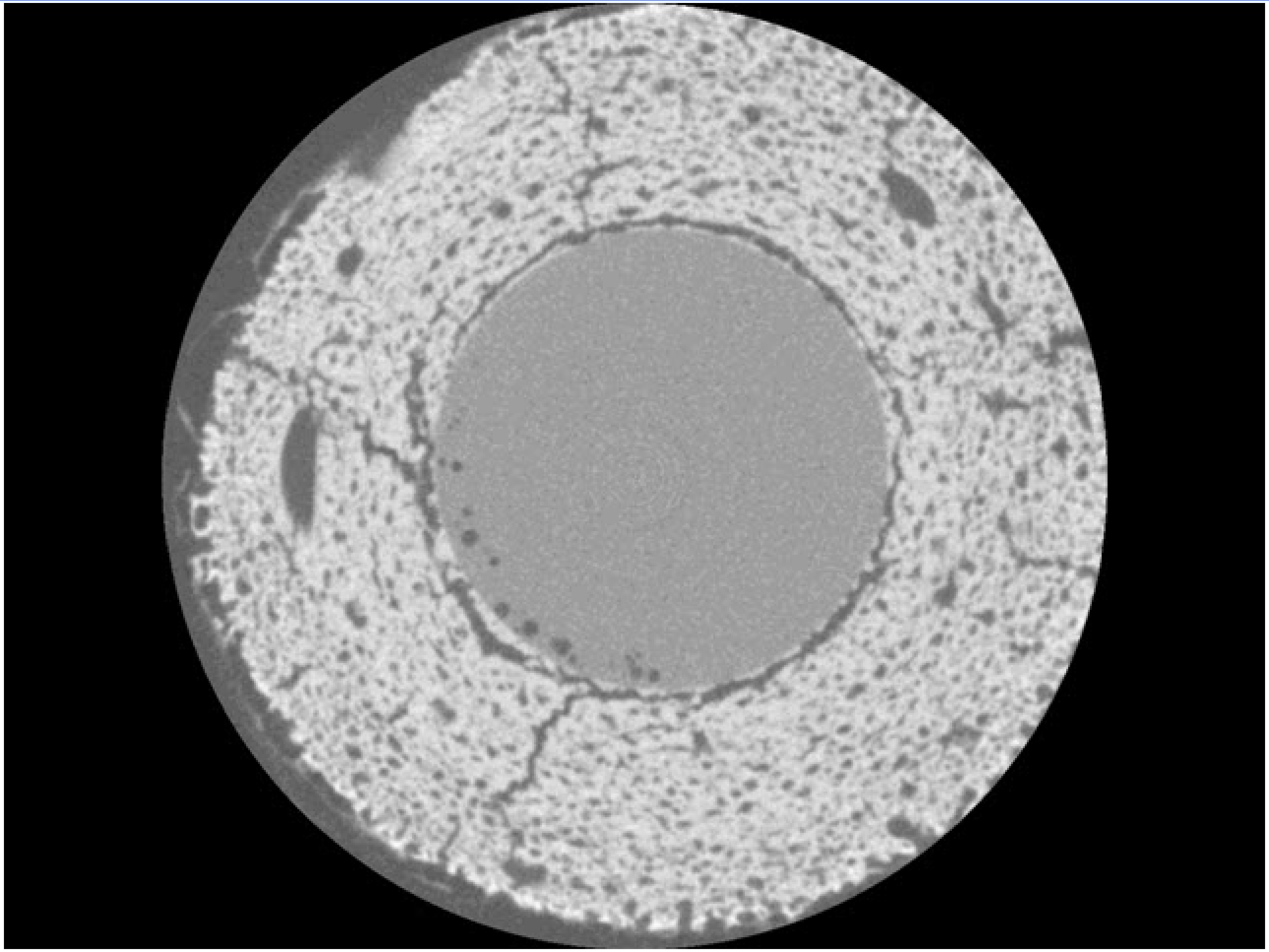
How Does Microstructure Relate to Thermal Conductivity?

- X-ray microtomography
  - Inherently three-dimensional
  - Intensity of signal based on x-ray transmission (local density) of material
  - Voxels dimensions of 10 μm readily available
    - 1 μm at specialized facilities (e.g., ESRF in France)
  - NIST has "imaged" a variety of FRMs in collaboration with the Center for Quantitative Imaging at Pennsylvania State University





X-ray Microtomography of Flame-Exposed Intumescent Coating FRM



From Center for Quantitative Imaging, Penn State Univ.

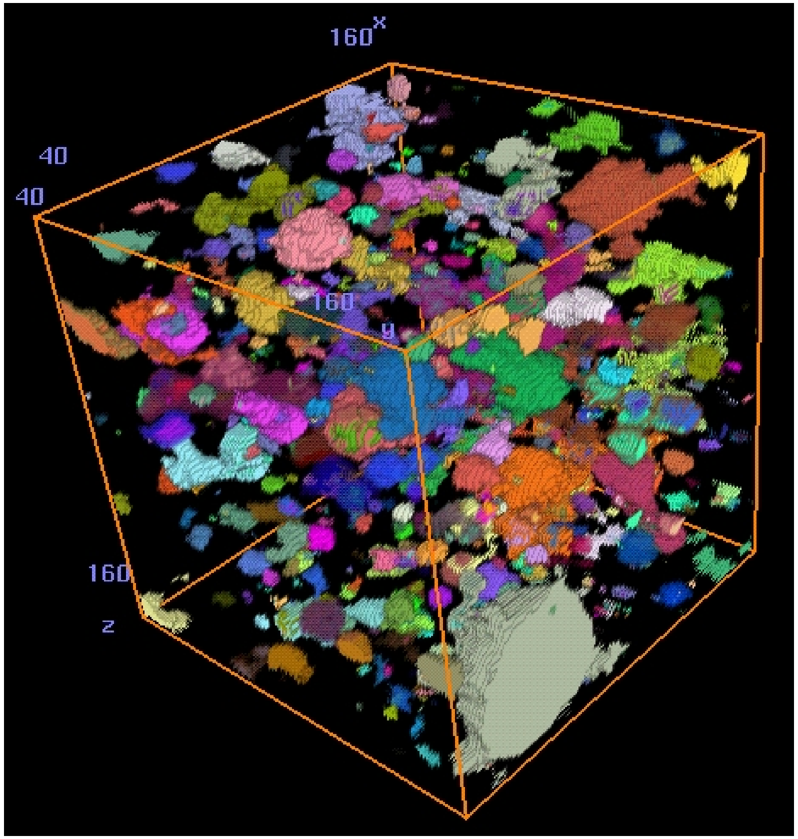
Microstructure → Thermal Conductivity

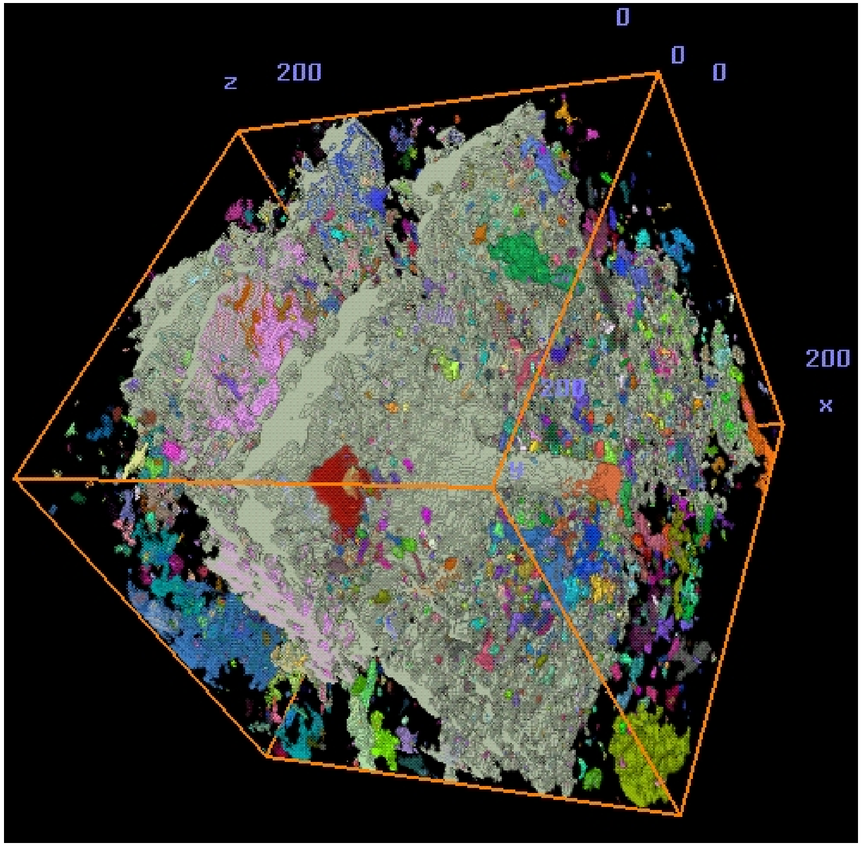
- Segment 3-D microstructures into pores and solids (binary image)
- Extract a 200x200x200 voxel subvolume from each microstructure data set
- Separate and quantify volume of each "pore" (erosion/dilation, watershed segmentation-Russ, 1988, *Acta Stereologica*)
- Input segmented subvolume into a finite difference program to compute thermal conductivity (compare to measured values)

Three-Dimensional X-ray Microtomography

Three-dimensional images of isolated pores

Gypsum-based	Fiber/cement-based





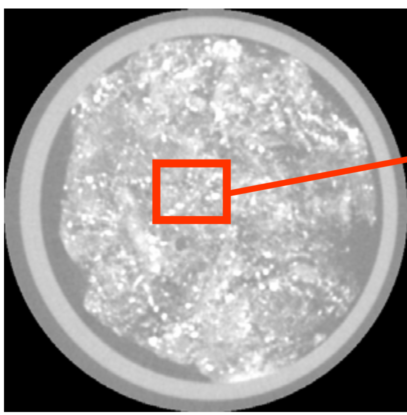
Thermal Conductivity Computation

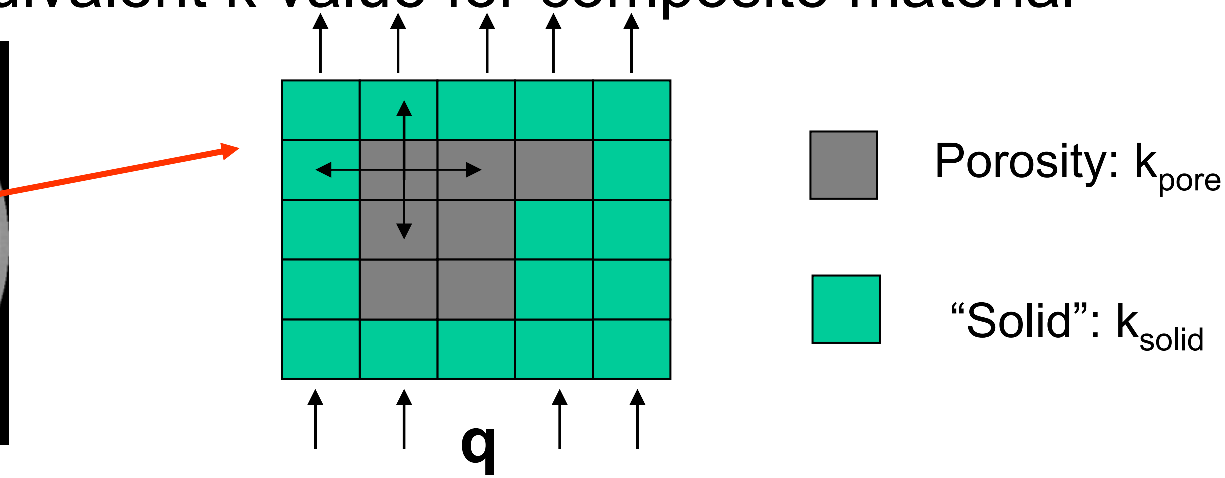
$$q = -kA\,(\partial T/\partial x)$$

-Use finite difference technique with conjugate gradient solver (Garboczi, 1998, **NISTIR 6269**)

-Put a temperature gradient across the sample and solve for heat flow at each node

-Compute equivalent k value for composite material

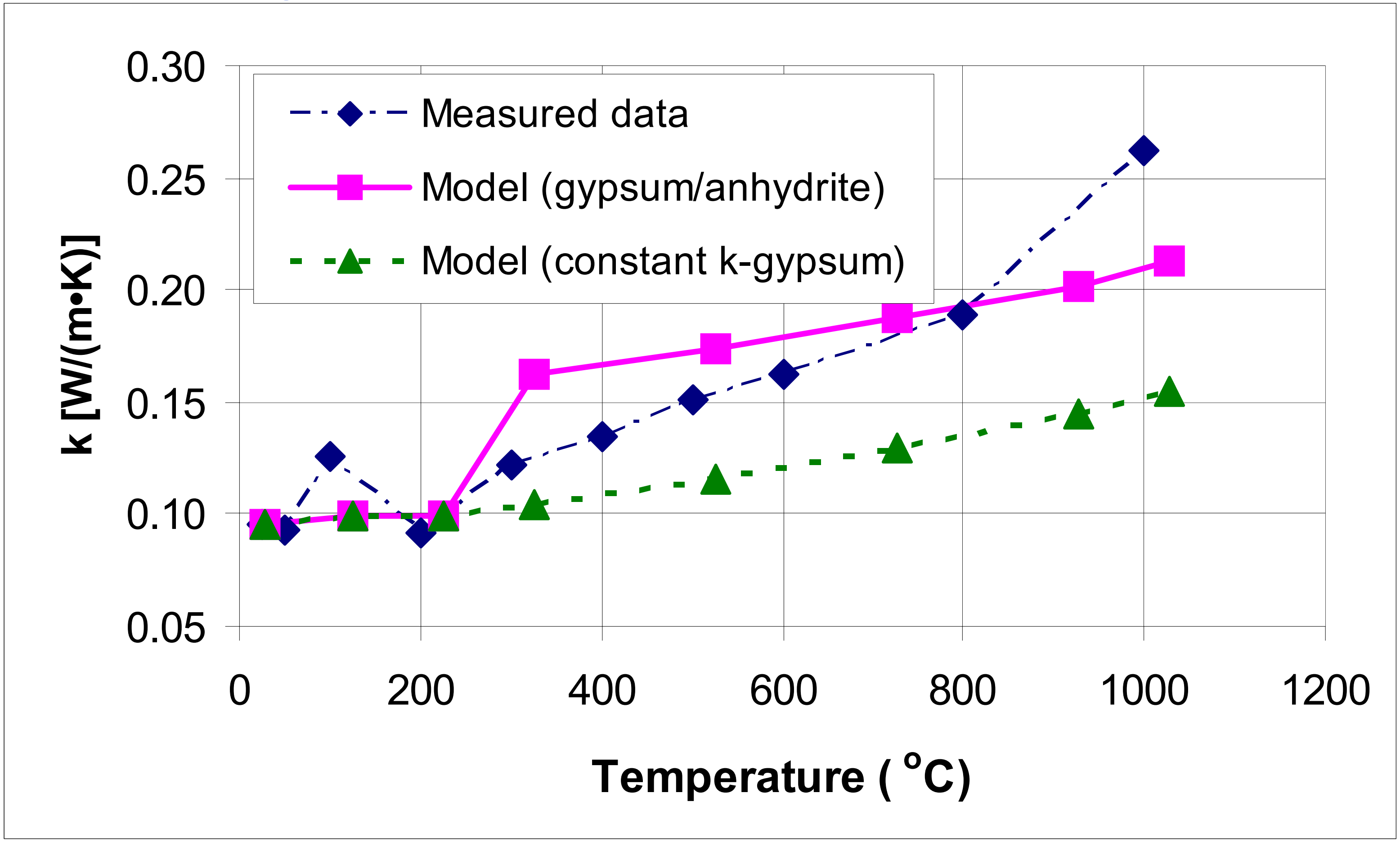




-Need to know values for k_{pore} and k_{solid} (itself microporous)

- Theory of Russell (1935) for porous media
- Theory of Loeb (1954) for radiation in spherical pores

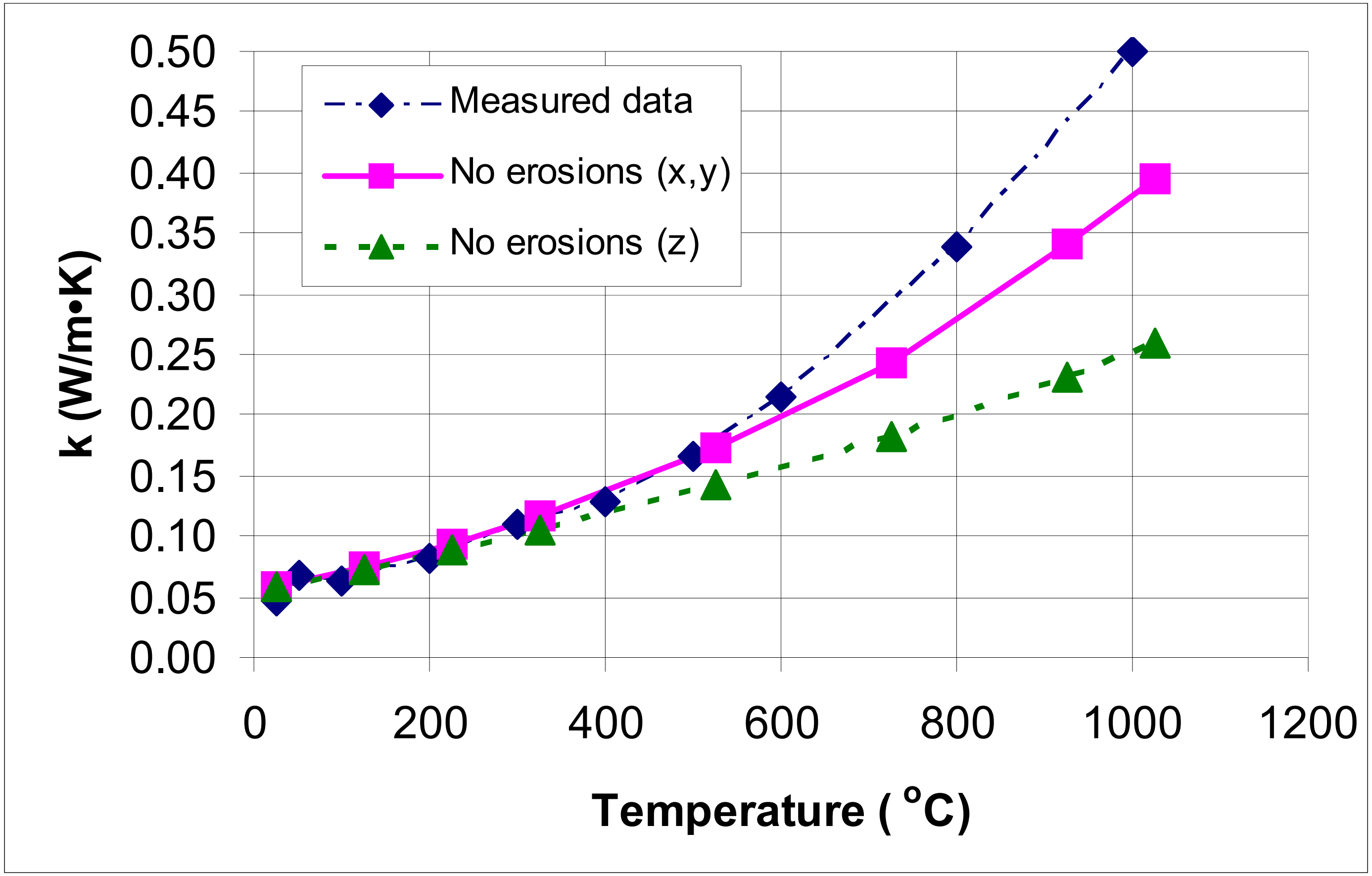
Microstructure Modeling Results: Gypsum-Based Material FRM C



Complication- gypsum to anhydrite conversion

$k_{gypsum} \approx 1.2$ W/m•K $k_{anhydrite} \approx 4.8$ W/m•K (Horai, 1971)

Microstructure Modeling Results: Fiber/Cement-Based Material FRM B



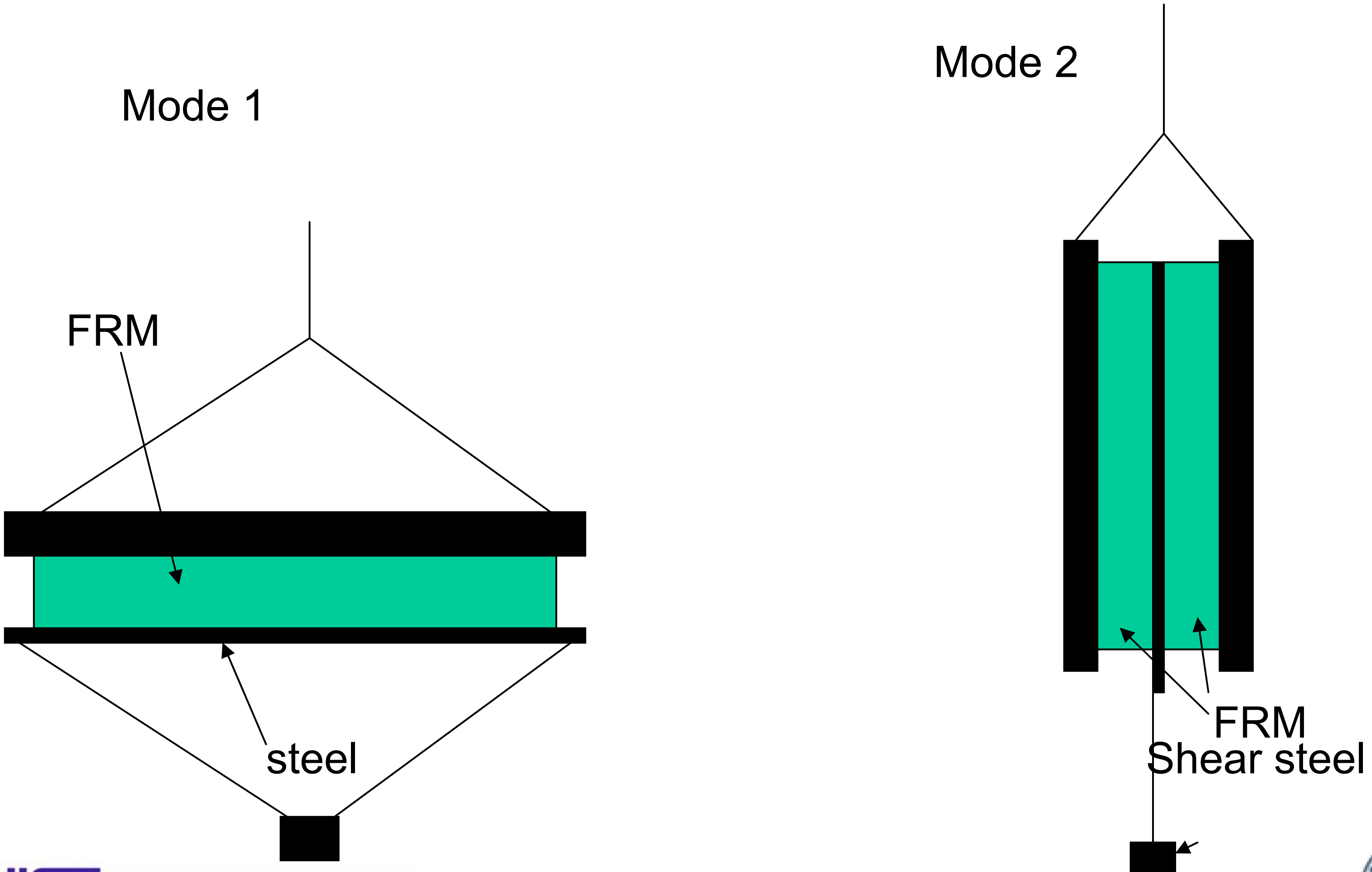
Complications

- Anisotropy of microstructure
- Radiation transfer through connected pores (Flynn and Gorthala, 1997)

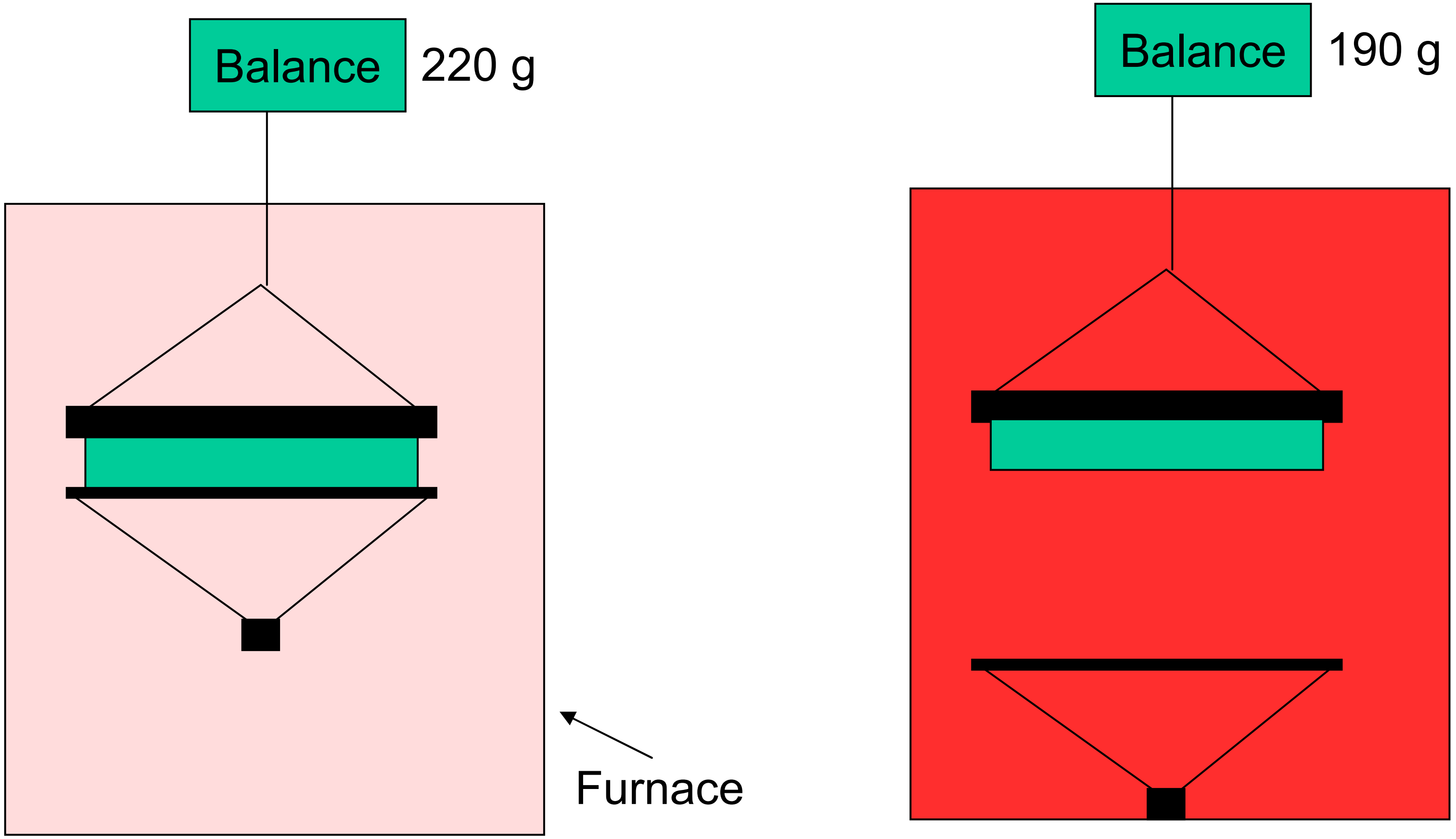
k vs. Porosity and Pore Size

FRM	ρ (kg/m³)	Porosity	Pore radius (mm)	k (23 °C) [W/(m•K)]	k (1000 °C) [W/(m•K)]
A-fiber	313.7	87.5 %	0.5	0.0534	0.3708
B-fiber	236.8	**91.2 %**	0.75	**0.0460**	0.5010
C-gypsum	292.4	87.2 %	**0.2**	0.0954	**0.2618**

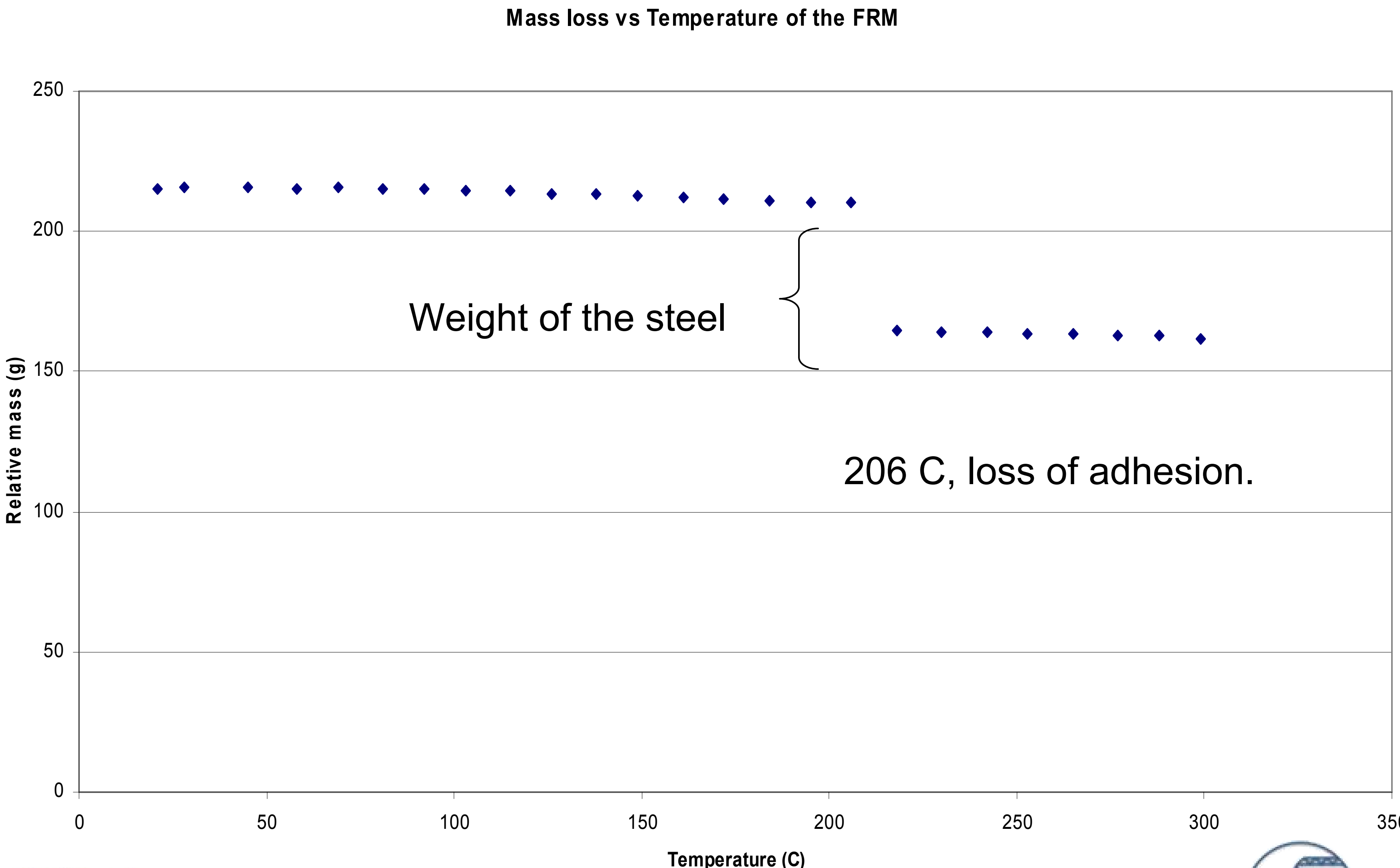
What is the temperature dependence of the adhesion?



Instrument Design



Gypsum-based material, Mode 1



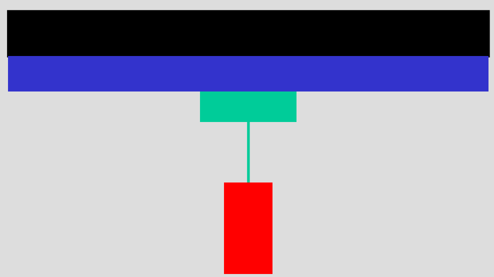
Both Adhesive and Cohesive Failure

Intumescent Material

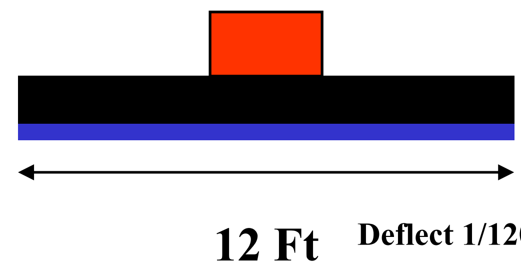
Cohesive failure of the material, but the steel remained covered.

Other current FRM Standards:

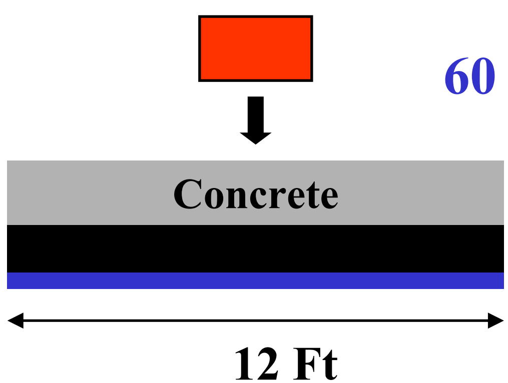
- ASTM E736 (Cohesive/Adhesive)



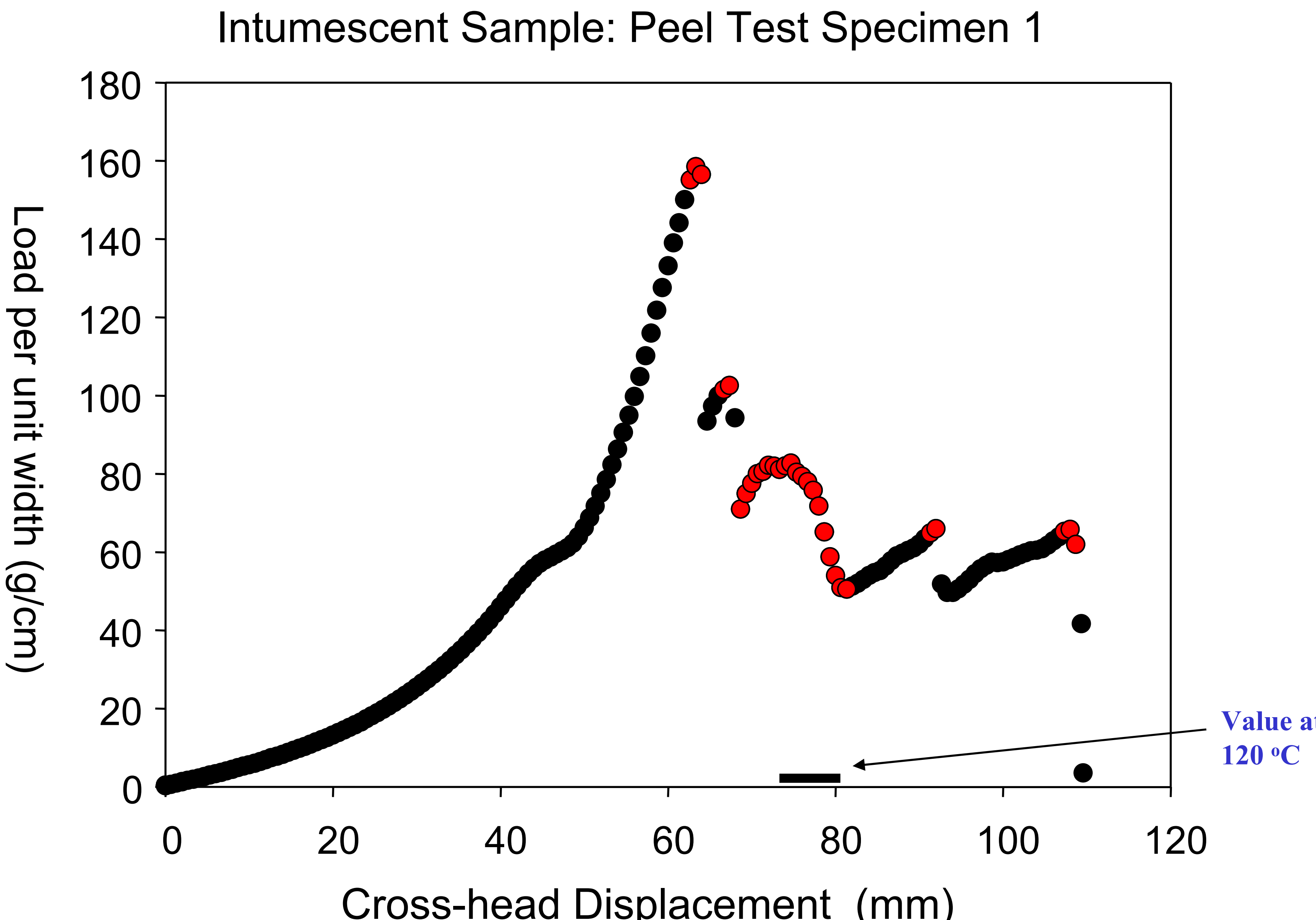
ASTM E759 (Effect of Deflection)

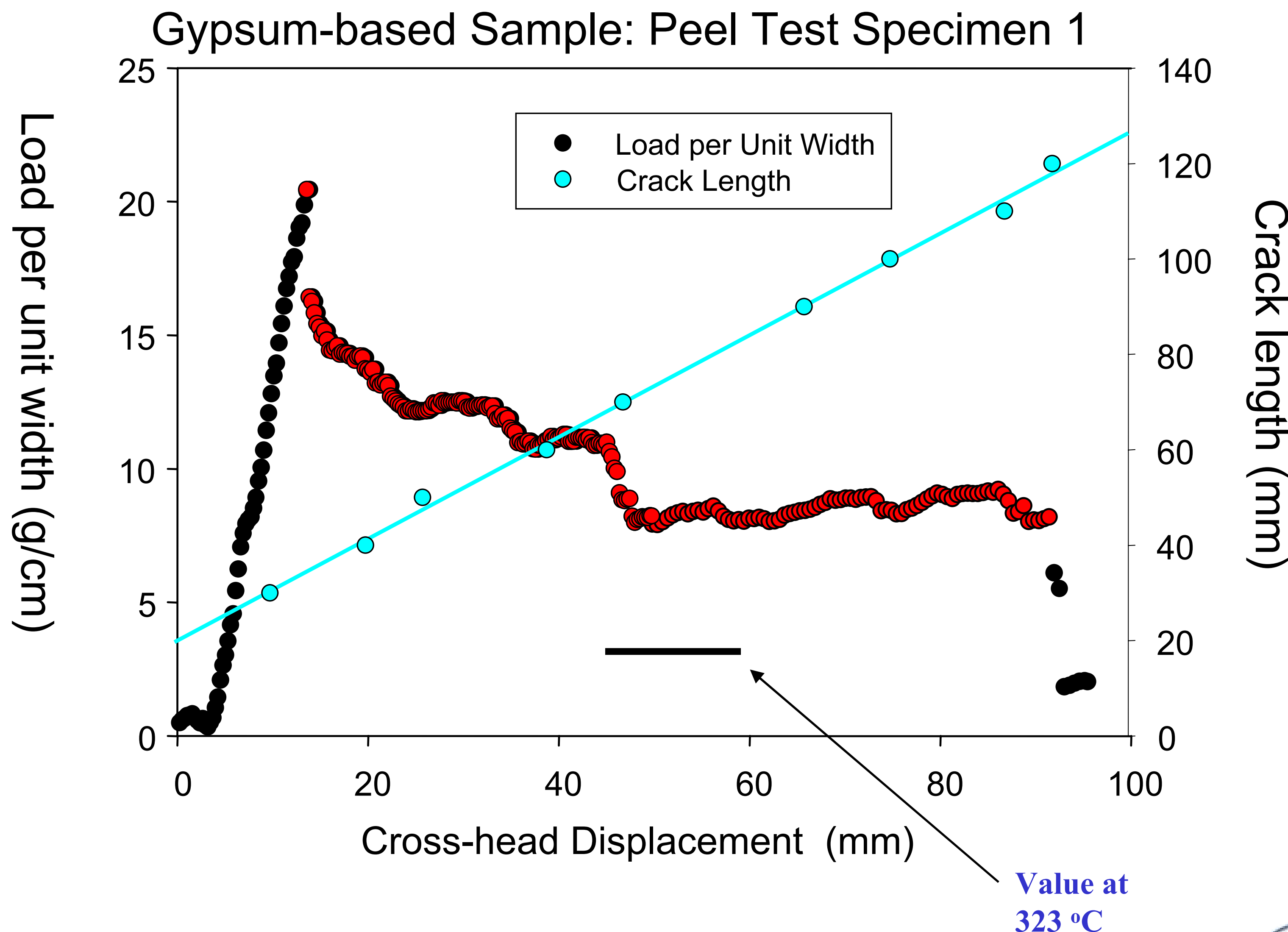


- ASTM E760 (Effect of Impact)



60 lb from 4 ft.


Intumescent Sample: Peel Test Specimen 1
180
160
140
120
100
80
60
40
20
0
Load per unit width (g/cm)
0
20
40
60
80
100
120
Cross-head Displacement (mm)
Value at
120 °C


Gypsum-based Sample: Peel Test Specimen 1
Load per Unit Width
Crack Length
Load per unit width (g/cm)
Crack length (mm)
Cross-head Displacement (mm)
0
5
10
15
20
25
0
20
40
60
80
100
120
140
0
20
40
60
80
100
Value at
323 °C

Summary

- Slug calorimeter setup provides a low cost and efficient method to characterize the thermal performance of FRMs
  - Temperature range of room temperature to 700 ^{o}C
  - Influences of reactions, phase changes, and mass transfer can be determined by using multiple heating/cooling cycles
- 3-D microstructure of FRMs can be captured and quantified using x-ray microtomography
- Both total porosity (density) and pore size are critical to the thermal performance of FRMs
  - These parameters have already been optimized for high temperature insulation boards, but not yet for FRMs
- Adhesion properties are significantly different at room temperature and elevated temperatures

Outreach and Technology Transfer

- New section of electronic monograph on FRMs
  - http://ciks.cbt.nist.gov/monograph
  - Separate chapters on microstructure, adhesion, and thermophysical properties
- BFRL/industry consortium formed 03/06
  - http://ciks.cbt.nist.gov/~bentz/FRMconsortium.html
  - Six industrial members each contributing $20 K
  - Initial scope of 2 years
- Initiating standardization efforts for the slug calorimeter test method (in ASTM E37 – Thermal Measurements)
  - Also serving on UL STP 263 where the first of its kind durability standard is being developed for FRMs